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(54) Abstract Title Stabilizer mixtures comprising a sterically hindered amine

(57) A stabilizer mixture contains

(A) a sterically hindered amine compound, and

(B) two different compounds selected from an organic selt of Zn, an inorganic selt of Zn, an organic selt of Mg and an inorganic salt of Mg; the weight ratio of the two different compounds being 1:10 to 10:1; with the provisos that

(1) the stabilizer mixture is essentially free of perchloric acid, and

(2) the two compounds in component (B) are different from the combination ZnO and Zn stearate and the combination ZnO and hydrotalcite; is useful for stabilizing an organic material, in particular a polyolefin, against degradation induced by light, heat or oxidation.

Also claimed is a composition comprising an organic material and a stabilizer mixture comprising (A) and (B) with the proviso that the composition is essentially free of perchloric acid.

The inorganic salt may be an oxide or hydroxide.

Stabilizer mixture

The present invention relates to a stabilizer mixture containing a sterically hindered amine compound and two different Mg- and/or Zn-compounds, the use of this mixture for stabilizing an organic material, in particular a polyolefin, against degradation induced by light, heat or oxidation and the organic material thus stabilized.

The stabilization of polyolefins is described in numerous publications, for example in US-A-4,929,652, US-A-5,025,051, US-A-5,037,870, EP-A-276,923, EP-A-290,388, EP-A-429,731, EP-A-468,923, EP-A-661,341, EP-A-690,094, DE-A-19,545,896 (Derwent 96-278,994/29; Chemical Abstracts 125:116779q), WO-A-95/25,767, GB-A-2,293,827 and Chemical Abstracts 106:197407z.

In more detail, the present invention relates to a stabilizer mixture containing

- (A) a sterically hindered amine compound, and
- (B) two different compounds selected from the group consisting of an organic salt of Zn, an Inorganic salt of Zn, an organic salt of Mg and an inorganic salt of Mg; the weight ratio of the two different compounds being 1:10 to 10:1; with the provisos that
- (1) the stabilizer mixture is essentially free of perchloric acid, and
- (2) the two compounds in component (B) are different from the combination ZnO and Zn stearate and the combination ZnO and hydrotalcite.

The weight ratio of the two different compounds of component (B) is preferably 1:5 to 5:1, in particular 1:2 to 2:1.

The sterically hindered amine is preferably a compound containing at least one group of the formula (I) or (II)

$$G-CH_{2} \xrightarrow{CH_{3}} G_{2}$$

$$G-CH_{2} \xrightarrow{CH_{3}} G_{3}$$

$$G-CH_{2} \xrightarrow{CH_{3}} G_{3}$$

in which G is hydrogen or methyl, and G_1 and G_2 , independently of one another, are hydrogen, methyl or together are a substituent =0.

More detailed examples of sterically hindered amines are described below under classes (a') to (i').

(a') A compound of the formula (la)

$$\begin{bmatrix}G-CH_2&G_1\\G_{11}&N&G_1\\G-CH_2&CH_3&\end{bmatrix}_{n_1}$$
 (la)

in which n_1 is a number from 1 to 4, G and G_1 , independently of one another, are hydrogen or methyl,

G₁₁ is hydrogen, Oʻ, hydroxyl, C₁-C₁₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, C₇-C₁₂aralkyl, C₁-C₁₈alkoxy, C₅-C₈cycloalkoxy, C₇-C₉phenylalkoxy, C₁-C₈alkanoyl, C₃-C₅alkenoyl, C₁-C₁₈alkanoyloxy, glycidyl or a group of the formula -CH₂CH(OH)-Z, in which Z is hydrogen, methyl or phenyl, G₁₁ preferably being H, C₁-C₄alkyl, allyl, benzyl, acetyl or acryloyl, and G₁₂, if n₁ is 1, is hydrogen, C₁-C₁₈alkyl which is uninterrupted or interrupted by one or more oxygen atoms, cyanoethyl, benzoyl, glycidyl, a monovalent radical or an aliphatic, cycloaliphatic, araliphatic, unsaturated or aromatic carboxylic acid, carbamic acid or phosphorus-containing acid or a monovalent silyl radical, preferably a radical of an aliphatic

carboxylic acid having 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid having 7 to 15 carbon atoms, or an α,β-unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms, where each carboxylic acid can be substituted in the aliphatic, cycloaliphatic or aromatic molety by 1 to 3 -COOZ₁₂ groups, in which Z₁₂ is H, C₁-C₂₀alkyl, C₃-C₁₂alkenyl, C₅-C₇cycloalkyl, phenyl or benzyl, G₁₂, if n₁ is 2, is C₂-C₁₂alkylene. C₄-C₁₂alkenylene, xylylene, a divalent redical of an aliphatic

G₁₂, if n₁ is 2, is C₂-C₁₂alkylene, C₄-C₁₂alkenylene, xylylene, a divalent radical of an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid, dicarbamic acid or phosphorus-containing acid or a divalent silyl radical, preferably a radical of an aliphatic dicarboxylic acid having 2 to 36 carbon atoms, or a cycloaliphatic or aromatic dicarboxylic acid having 8-14 carbon atoms or of an aliphatic, cycloaliphatic or aromatic dicarbamic acid having 8-14 carbon atoms, where each dicarboxylic acid may be substituted in the aliphatic, cycloaliphatic or aromatic molety by one or two -COOZ₁₂ groups,

G₁₂, if n₁ is 3, is a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid, which may be substituted in the aliphatic, cycloaliphatic or aromatic molety by -COOZ₁₂, of an aromatic tricarbamic acid or of a phosphorus-containing acid, or is a trivalent silyl radical,

and G_{12} , if n_1 is 4, is a tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid.

The carboxylic acid radicals mentioned above are in each case taken to mean radicals of the formula $(-CO)_xR$, where x is as defined above, and the meaning of R arises from the definition given.

Alkyl with up to 20 carbon atoms is, for example, methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

 C_3 - C_8 alkenyl G_{11} can be, for example, 1-propenyl, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl, 2-octenyl, or 4-tert-butyl-2-butenyl.

C₃-C₈alkynyl G₁₁ is preferably propargyl.

C7-C12aralkyl G11 is, in particular, phenethyl, especially benzyl.

C₁-C₁₈alkoxy G₁₁ is, for example, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, pentoxy, isopentoxy, hexoxy, heptoxy, octoxy, decyloxy, dodecyloxy, tetradecyloxy, hexadecyloxy and octadecyloxy. C₅-C₁₂alkoxy, in particular heptoxy and octoxy, is preferred.

 C_5 - C_8 cycloalkoxy G_{11} is, for example, cyclopentoxy, cyclohexoxy, cyclohexoxy, cyclohexoxy, cyclohexoxy, cyclohexoxy, in particular cyclopentoxy and cyclohexoxy, is preferred.

C₇-C₉phenyialkoxy is, for example, benzyloxy.

 C_1 - C_8 alkanoyl G_{11} is, for example, formyl, propionyl, butyryl, octanoyl, but preferably acetyl and C_3 - C_5 alkenoyl G_{11} is in particular acryloyl.

 C_1 - C_{18} alkanoyloxy G_{11} is, for example, formyloxy, acetyloxy, propionyloxy, butyryloxy, valeryloxy, lauroyloxy, palmitoyloxy and stearoyloxy.

Examples of several G₁₂ radicals are given below.

If G_{12} is a monovalent radical of a carboxylic acid, it is, for example, an acetyl, caproyl, stearoyl, acryloyl, methacryloyl, benzoyl or β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl radical.

If G_{12} is a monovalent silyl radical, it is, for example, a radical of the formula $-(C_iH_{2i})-Si(Z')_2Z''$, in which j is an Integer in the range from 2 to 5, and Z' and Z'', independently of one another, are C_1-C_4 alkyl or C_1-C_4 alkoxy.

If G₁₂ is a divalent radical of a dicarboxylic acid, it is, for example, a malonyl, succinyl, glutaryl, adipoyl, suberoyl, sebacoyl, maleoyl, itaconyl, phthaloyl, dibutylmalonyl, dibenzylmalonyl, butyl(3,5-di-tert-butyl-4-hydroxybenzyl)malonyl or bicycloheptenedicarbonyl radical or a group of the formula

If G_{12} is a trivalent radical of a tricarboxylic acid, it is, for example, a trimellitoyl, citryl or nitrilotriacetyl radical.

If G_{12} is a tetravalent radical of a tetracarboxylic acid, it is, for example, the tetravalent radical of butane-1,2,3,4-tetracarboxylic acid or of pyromellitic acid.

If G_{12} is a divalent radical of a dicarbamic acid, it is, for example, hexamethylenedicarbamoyl or 2,4-toluylenedicarbamoyl radical.

Preference is given to compounds of the formula (Ia) in which G and G_1 are hydrogen, G_{11} is hydrogen or methyl, n_1 is 2 and G_{12} is the diacyl radical of an aliphatic dicarboxylic acid having 4-12 carbon atoms.

Examples of polyalkylpiperidine compounds from this class are the following compounds:

- 1) 4-hydroxy-2,2,6,6-tetramethylpiperidine
- 2) 1-allyl-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 3) 1-benzyl-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 4) 1-(4-tert-butyl-2-butenyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 5) 4-stearoyloxy-2,2,6,6-tetramethylpiperidine
- 6) 1-ethyl-4-salicyloyloxy-2,2,6,6-tetramethylpiperidine
- 7) 4-methacryloyloxy-1,2,2,6,6-pentamethylpiperidine
- 8) 1,2,2,6,6-pentamethylpiperidin-4-yl β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate
- 9) di(1-benzyl-2,2,6,6-tetramethylpiperidin-4-yl) maleate

- 10) di(2,2,6,6-tetramethylpiperidin-4-yl) succinate
- 11) di(2,2,6,6-tetramethylpiperidin-4-yl) glutarate
- 12) di(2,2,6,6-tetramethylplperidin-4-yl) adipate
- 13) di(2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 14) di(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate
- 15) di(1,2,3,6-tetramethyl-2,6-diethyl-piperidin-4-yl) sebacate
- 16) di(1-allyl-2,2,6,6-tetramethylpiperidin-4-yl) phthalate
- 17) 1-hydroxy-4-ß-cyanoethoxy-2,2,6,6-tetramethylpiperidine
- 18) 1-acetyl-2,2,6,6-tetramethylpiperidin-4-yl acetate
- 19) tri(2,2,6,6-tetramethylpiperidin-4-yl) trimellitate
- 20) 1-acryloyl-4-benzyloxy-2,2,6,6-tetramethylpiperidine
- 21) di(2,2,6,6-tetramethylpiperidin-4-yl) diethylmalonate
- 22) di(1,2,2,6,6-pentamethylpiperidin-4-yl) dibutylmalonate
- 23) di(1,2,2,6,6-pentamethylplperidin-4-yl) butyl(3,5-di-tert-butyl-4-hydroxybenzyl)malonate
- 24) di(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 25) di(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 26) hexane-1',6'-bis(4-carbamoyloxy-1-n-butyl-2,2,6,6-tetramethylpiperidine)
- 27) toluene-2',4'-bis-(4-carbamoyloxy-1-n-propyl-2,2,6,6-tetramethylpiperidine)
- 28) dimethylbis(2,2,6,6-tetramethylpiperidin-4-oxy)silane
- 29) phenyltris(2,2,6,6-tetramethylpiperidin-4-oxy)silane
- 30) tris(1-propyl-2,2,6,6-tetramethylpiperidin-4-yl) phosphite
- 30-a) trls(1-methyl-2,2,6,6-tetramethylpiperidin-4-yl) phosphite
- 31) tris(1-propyl-2,2,6,6-tetramethylpiperidin-4-yl) phosphate
- 32) phenyl bis(1,2,2,6,6-pentamethylplperidin-4-yl) phosphonate
- 33) 4-hydroxy-1,2,2,6,6-pentamethylpiperidine
- 34) 4-hydroxy-N-hydroxyethyl-2,2,6,6-tetramethylpiperidine
- 35) 4-hydroxy-N-(2-hydroxypropyl)-2,2,6,6-tetramethylpiperidine
- 36) 1-glycidyl-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 36-a) 1,2,3,4-tetrakis[2,2,6,6-tetramethylplperidin-4-yloxycarbonyl]butane
- 36-b) 1,2,3,4-tetrakis[1,2,2,6,6-pentamethylpiperidin-4-yloxycarbonyi]butane
- 36-c) 2,2,6,6-tetramethylpiperidin-4-yloxycarbonyl(C₁₅-C₁₇alkane)

(b') A compound of the formula (lb)

$$\begin{bmatrix}
G - CH_2 & G_1 & G_{13} & G_{14} & G_{14} & G_{14} & G_{14} & G_{14} & G_{14} & G_{14}
\end{bmatrix}$$
(Ib)

in which n_2 is the number 1, 2 or 3, G, G_1 and G_{11} are as defined under (a'), G_{13} is hydrogen, C_1 - C_1 2alkyl, C_2 - C_5 hydroxyalkyl, C_5 - C_7 cycloalkyl, C_7 - C_8 aralkyl, C_1 - C_{18} alkanoyl, C_3 - C_5 alkenoyl, benzoyl or a group of the formula

and G₁₄, if n₂ is 1, is hydrogen, C₁-C₁₈alkyl, C₃-C₈alkenyl, C₅-C₇cycloalkyl, C₁-C₄alkyl which is substituted by a hydroxyl, cyano, alkoxycarbonyl or carbamide group, glycidyl, a group of the formula -CH₂-CH(OH)-Z or of the formula -CONH-Z, in which Z is hydrogen, methyl or phenyl;

G₁₄, if n₂ is 2, is C₂-C₁₂alkylene, C₆-C₁₂arylene, xylylene, a -CH₂-CH(OH)-CH₂ group or a -CH₂-CH(OH)-CH₂-O-D-O- group, in which D is C₂-C₁₀alkylene, C₆-C₁₅arylene, C₆-C₁₂cycloalkylene, or, provided that G₁₃ is not alkanoyl, alkenoyl or benzoyl, G₁₄ can alternatively be 1-oxo-C₂-C₁₂alkylene, a divalent radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid or alternatively the group -CO-, G₁₄, if n₂ is 3, is a group

or, if n_2 is 1, G_{13} and G_{14} together can be the divalent radical of an aliphatic, cycloaliphatic or aromatic 1,2- or 1,3-dicarboxylic acid.

Some examples for the radicals G₁₃, G₁₄ and D are given below.

Any alkyl substituents are as defined above for (a').

Any C5-C7cycloalkyl substituents are, in particular, cyclohexyl.

 C_7 - C_8 aralkyl G_{13} is, in particular, phenylethyl or especially benzyl.

 C_2 - C_5 hydroxyalkyl G_{13} is, in particular, 2-hydroxyethyl or 2-hydroxypropyl.

 C_1 - C_{10} alkanoyi G_{13} is, for example, formyl, acetyl, propionyl, butyryl, octanoyl, dodecanoyl, hexadecanoyl, octadecanoyl, but preferably acetyl, and C_3 - C_5 alkenoyl G_{13} is, in particular, acryloyl.

 C_2 - C_8 alkenyl G_{14} is, for example, aliyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl or 2-octenyl.

 G_{14} as a hydroxyl-, cyano-, alkoxycarbonyl- or carbamide-substituted C_1 - C_4 alkyl can be, for example, 2-hydroxyethyl, 2-hydroxypropyl, 2-cyanoethyl, methoxycarbonylmethyl, 2-ethoxycarbonylethyl, 2-aminocarbonylpropyl or 2-(dimethylaminocarbonyl)ethyl.

Any C2-C12alkylene radicals are, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

Any C_6 - C_{15} arylene substituents are, for example, o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

C₆-C₁₂cycloalkylene is, in particular, cyclohexylene.

G₁₄ as 1-oxo-C₂-C₁₂alkylene is preferably a group

Preference is given to compounds of the formula (lb) in which n_2 is 1 or 2, G and G_1 are hydrogen, G_{11} is hydrogen or methyl, G_{13} is hydrogen, C_1 - C_{12} alkyl or a group of the formula

and G_{14} , in the case where n=1, is hydrogen or C_1 - C_{12} alkyl, and, in the case where n=2, is C_2 - C_8 alkylene or 1-oxo- C_2 - C_8 alkylene.

Examples of polyalkylplperidine compounds from this class are the following compounds:

- 37) N,N'-bis(2,2,6,6-tetramethylplperidin-4-yl)hexamethylene-1,6-diamine
- 38) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylene-1,6-diacetamide
- 39) bis(2,2,6,6-tetramethylpiperidin-4-yl)amine
- 40) 4-benzoylamino-2,2,6,6-tetramethylpiperidine
- 41) N,N'-bis(2,2,6,6-tetramethylplperidin-4-yl)-N,N'-dibutyladipamide
- 42) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yi)-N,N'-dicyclohexyi-2-hydroxypropylene-1.3-diamine
- 43) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)-p-xylylenediamine
- 44) N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)succinamide
- 45) bis(2,2,6,6-tetramethylpiperidin-4-yl) N-(2,2,6,6-tetramethylpiperidin-4-yl)-8-aminodipropionate
- 46) The compound of the formula

1

$$\begin{bmatrix} H_3C & CH_3 & n-C_4H_9 & OH \\ H_3C & N-CH_2-CH-CH_2-O & CH_3 \\ H_3C & CH_3 & CH_3 \\ \end{bmatrix}$$

- 47) 4-(bis-2-hydroxyethylamino)-1,2,2,6,6-pentamethylpiperidine
- 48) 4-(3-methyl-4-hydroxy-5-tert-butyl-benzamido)-2,2,6,6-tetramethylpiperidine
- 49) 4-methacrylamido-1,2,2,6,6-pentamethylpiperidine

49-b) N,N',N"-tris[2,2,6,6-tetramethylpiperidin-4-ylamino(2-hydroxypropylene)]isocyanurate

49-c) 2-(2,2,6,6-tetramethylpiperidin-4-ylamino)-2-(2,2,6,6-tetramethylpiperidin-4-ylaminocarbonyl)propane

49-d) 1,6-bis[N-(2,2,6,6-tetramethylpiperidin-4-yl)formylamino]hexane

(c') A compound of the formula (Ic)

$$\begin{bmatrix}
G - CH_2 & G_1 & O \\
G_{11} - N & O & G_{15} & G_{16}
\end{bmatrix}$$

$$G - CH_2 & CH_3 & O & G_{15}$$

$$G - CH_2 & CH_3 & O & G_{15}$$

$$G - CH_2 & CH_3 & O & G_{15}$$

$$G - CH_2 & CH_3 & O & G_{15}$$

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$$G - CH_2 & CH_3 & O & G_{15}$$

$$G$$

in which n_3 is the number 1 or 2, G, G_1 and G_{11} are as defined under (a'), and G_{15} , if n_3 is 1, is C_2 - C_8 alkylene, C_2 - C_8 hydroxyalkylene or C_4 - C_{22} acyloxyalkylene, and if n_3 is 2, G_{15} is the $(-CH_2)_2C(CH_2-)_2$ group.

 C_2 - C_8 alkylene or C_2 - C_8 hydroxyalkylene G_{15} is, for example, ethylene, 1-methylethylene, propylene, 2-ethylpropylene or 2-ethyl-2-hydroxymethylpropylene.

 $C_4\text{--}C_{22}$ acyloxyalkylene G_{15} is, for example, 2-ethyl-2-acetoxymethylpropylene.

Examples of polyalkylpiperidine compounds from this class are the following compounds:

- 50) 9-aza-8,8,10,10-tetramethyl-1,5-dioxaspiro[5.5]undecane
- 51) 9-aza-8,8,10,10-tetramethyl-3-ethyl-1,5-dioxaspiro[5.5]undecane
- 52) 8-aza-2,7,7,8,9,9-hexamethyl-1,4-dioxaspiro[4.5]decane
- 53) 9-aza-3-hydroxymethyl-3-ethyl-8,8,9,10,10-pentamethyl-1,5-dioxaspiro[5.5]undecane
- 54) 9-aza-3-ethyl-3-acetoxymethyl-9-acetyl-8,8,10,10-tetramethyl-1,5-dioxaspiro[5.5]-undecane
- 55) 2,2,6,6-tetramethylpiperidine-4-spiro-2'-(1',3'-dioxane)-5'-spiro-5"-(1",3"-dioxane)-2"-spiro-4"'-(2"',2",6"',6"'-tetramethylpiperidine)
- (d') A compound of the formula (Id-1), (Id-2) or (Id-3),

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & G_{16} & O \\
G_{11} & N - C & O \\
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O \\
C - N - O & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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G - CH_{2} & CH_{3} & O & O
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$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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G - CH_{2} & CH_{3} & O & O
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G - CH_{2} & CH_{3} & O & O
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$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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G - CH_{2} & CH_{3} & O & O
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$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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G - CH_{2} & CH_{3} & O & O
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G - CH_{2} & CH_{3} & O & O
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G - CH_{2} & CH_{3} & O & O
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G - CH_{2} & CH_{3} & O & O
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$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
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$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{2} & CH_{3} & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{3} & CH_{3} & O & O
\end{bmatrix}$$

$$\begin{bmatrix}
G - CH_{3} & CH_{$$

$$G-CH_{2}$$

$$G_{11}$$

$$G-CH_{2}$$

$$G-CH_{3}$$

$$G-CH_{2}$$

$$G-CH_{3}$$

$$\begin{bmatrix} G - CH_2 & CH_3 & G_1 & 0 - C - T_2 \\ G - CH_2 & CH_3 & 0 & 0 \end{bmatrix}_{n_A}$$
 (Id-3)

in which n_4 is the number 1 or 2, G, G_1 and G_{11} are as defined under (a'), G_{16} is hydrogen, C_1 - C_{12} alkyl, allyl, benzyl, glycidyl or C_2 - C_6 alkoxyalkyl, and G_{17} , if n_4 is 1, is hydrogen, C_1 - C_{12} alkyl, C_3 - C_5 alkenyl, C_7 - C_9 aralkyl, C_5 - C_7 cycloalkyl, C_2 - C_6 alkoxyalkyl, C_6 - C_{10} aryl, glycidyl or a group of the formula -(CH₂)_p-COO-Q or -(CH₂)_p-O-CO-Q, in which p is 1 or 2, and Q is C_1 - C_4 alkyl or phenyl, and G_{17} , if n is 2, is C_2 - C_{12} alkylene, C_4 - C_{12} alkenylene, C_6 - C_{12} arylene, a group of the formula -CH₂-CH(OH)-CH₂-O-D'-O-CH₂-CH(OH)-CH₂-, in which D' is C_2 - C_{10} alkylene, C_6 - C_{15} arylene, C_6 - C_{12} cycloalkylene or a group of the formula -CH₂CH(OD")CH₂-(OCH₂-CH(OD")CH₂)₂-, in which D" is hydrogen, C_1 - C_{16} alkyl, allyl, benzyl, C_2 - C_{12} alkanoyl or benzoyl, C_1 - C_{16} alkyl-substituted C_6 - C_{10} aryl or C_7 - C_{9} aralkyl, or C_1 - C_{16} alkyl-substituted C_6 - C_{10} aryl or C_7 - C_{9} aralkyl, or C_1 - C_{16} Clakane ring.

A compound of the formula (Id-3) is preferred.

Some examples of the several variables in the formulae (Id-1), (Id-2) and (Id-3) are given below.

Any C₁-C₁₂alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

Any C₁-C₁₈alkyl substituents can be, for example, the abovementioned groups and in addition, for example, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

Any C₂-C₆alkoxyalkyl substituents are, for example, methoxymethyl, ethoxymethyl, propoxymethyl, tert-butoxymethyl, ethoxyethyl, ethoxypropyl, n-butoxyethyl, tert-butoxyethyl, isopropoxyethyl or propoxypropyl.

C₃-C₅alkenyl G₁₇ is, for example, 1-propenyl, allyl, methallyl, 2-butenyl or 2-pentenyl.

 C_7 - C_9 aralkyl G_{17} , T_1 and T_2 are, in particular, phenethyl or especially benzyl. If T_1 and T_2 together with the carbon atom form a cycloalkane ring, this can be, for example, a cyclopentane, cyclohexane, cyclooctane or cyclododecane ring.

C₂-C₄hydroxyalkyl G₁₇ is, for example, 2-hydroxyethyl, 2-hydroxypropyl, 2-hydroxybutyl or 4-hydroxybutyl.

 C_6 - C_{10} aryl G_{17} , T_1 and T_2 are, in particular, phenyl or α - or β -naphthyl, which are unsubstituted or substituted by halogen or C_1 - C_4 alkyl.

C₂-C₁₂alkylene G₁₇ is, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

C₄-C₁₂alkenylene G₁₇ is, in particular, 2-butenylene, 2-pentenylene or 3-hexenylene.

 C_{6} - C_{12} arylene G_{17} is, for example, o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

C₂-C₁₂alkanoyl D" is, for example, propionyl, butyryl, octanoyl, dodecanoyl, but preferably acetyl.

 C_2 - C_{10} alkylene, C_6 - C_{15} arylene or C_6 - C_{12} cycloalkylene D' have, for example, one of the definitions given for D under (b').

Examples of polyalkylpiperidine compounds from this class are the following

56) 3-benzyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4

1

1

57) 3-n-octyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4-0

- 58) 3-allyl-1,3,8-triaza-1,7,7,9,9-pentamethylspiro[4.5]decane-2,4-dione
- 59) 3-glycidyl-1,3,8-triaza-7,7,8,9,9-pentamethylspiro[4.5]decane-2,4-dione
- 60) 1,3,7,7,8,9,9-heptamethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione
- 61) 2-isopropyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane
- 62) 2,2-dibutyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane
- 63) 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-21-oxodispiro[5.1.11.2]heneicosane
- 64) 2-butyl-7,7,9,9-tetramethyl-1-oxa-4,8-diaza-3-oxospiro[4.5]decane and preferably:
- 65) 8-acetyl-3-dodecyi-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4-dione

and the compounds of the following formulae:

66)
$$\begin{bmatrix} CH_3 & H & O \\ H_3C & N & CH_2 & OH \\ H_3C & CH_3 & O & CH_2 & CH - CH_2 - O - CH_2 & CH - OH \\ CH_3 & O & OH & CH_3 & CH - OH & CH_3 & OH & CH_3 & CH - OH & CH_3 &$$

67)
$$\begin{bmatrix} H_{3}C & H_{3} & H_{3}C & H_{3}$$

(e') A compound of the formula (le)

in which n_5 is the number 1 or 2, and G_{18} is a group of the formula

$$G-CH_{2}$$

$$G_{11}$$

$$G-CH_{2}$$

$$G_{11}$$

$$G-CH_{2}$$

$$G-CH_{2}$$

$$G-CH_{2}$$

$$G-CH_{2}$$

$$G-CH_{3}$$

$$G-CH_{2}$$

$$G-CH_{3}$$

$$G-CH_{3}$$

$$G-CH_{3}$$

$$G-CH_{3}$$

in which G and G_{11} are as defined under (a'), and G_{1} and G_{2} are hydrogen, methyl or, together, are a substituent =0,

E is -O- or -ND"-,

A is C2-C6alkylene or -(CH2)3-O- and

 x_1 is the number 0 or 1.

D" is hydrogen, C₁-C₁₂alkyl, C₂-C₅hydroxyalkyl or C₅-C₇cycloalkyl,

 G_{19} is identical to G_{18} or is one of the groups -N(G_{21})(G_{22}), -OG₂₃, -N(H)(CH₂OG₂₃) or -N(CH₂OG₂₃)₂,

 G_{20} , if n=1, is identical to G_{18} or G_{19} and, if n=2, is an -E-D^N-E- group, in which D^N is C_2 - C_8 alkylene or C_2 - C_8 alkylene which is interrupted by 1 or 2 -NG₂₁- groups, G_{21} is C_1 - C_{12} alkyl, cyclohexyl, benzyl or C_1 - C_4 -hydroxyalkyl or a group of the formula

Some examples of the several variables in the formula (le) are given below.

Any C₁-C₁₂alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

Any hydroxyalkyl substituents are, for example, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxybutyl or 4-hydroxybutyl.

Any C_5 - C_7 cycloalkyl substituents are, for example, cyclopentyl, cyclohexyl or cycloheptyl. Cyclohexyl is preferred.

 C_2 - C_6 alkylene A is, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene or hexamethylene.

If G_{21} and G_{22} together are C_4 - C_5 alkylene or oxaalkylene, they are, for example, tetramethylene, pentamethylene or 3-oxapentamethylene.

Examples of polyalkylpiperidine compounds from this class are the compounds of the following formulae:

71)
$$CH_3CH_2-N$$
 H_3C
 CH_3
 CH_3

72)
$$H_3C$$
 CH_3 $CH_$

where R is
$$H-N$$
 H_3C CH_3 CH_3 CH_3 $N-H$ N

where R' has the same meaning as in compound 76.

H₃C
$$H_3$$
C H_3 C H_4 C H_5 C H

(f') A compound of the formula (If)

wherein G₁₁ is as defined under (a').

A preferred example from this class is the following compound:

(g') Oligomeric or polymeric compounds whose recurring structural unit contains a 2,2,6,6-tetraalkylpiperidinyl radical, in particular polyesters, polyethers, polyamides, polyamines, polyurethanes, polyureas, polyureas, polyureas, poly(meth)acrylates, poly(meth)acrylates and copolymers thereof which contain such radicals.

Examples of 2,2,6,6-polyalkylpiperidine compounds from this class are the compounds of the following formulae, where m_1 to m_{14} is a number from 2 to about 200, preferably 2 to 100, for example 2 to 50, 2 to 40 or 3 to 40 or 4 to 10.

The meanings of the end groups which saturate the free valences in the oligomeric or polymeric compounds listed below depend on the processes used for the preparation of said compounds. The end groups can also in addition be modified after the synthesis of the compounds.

In the compounds 81 and 82, the end group bonded to the -O- can be, for example, hydrogen or a group -CO-(CH₂)₂-COO-Y or -CO-(CH₂)₄-COO-Y, respectively, with Y being hydrogen or C₁-C₄alkyl and the end group bonded to the diacyl can be, for example, -O-Y or a group

In the compound 83, the end group bonded to the amino residue can be, for example, a

for example, Cl.

In the compounds 84-1 and 84-2, the end group bonded to the triazine residue can be, for example, chlorine or a group

and the end group bonded to the diamino group can be, for example, hydrogen or a group

It may be convenient to replace the chlorine attached to the triazine by e.g. -OH or an amino group. Suitable amino groups are typically: pyrrolidin-1-yl, morpholino, -NH₂, -N(C₁-C₈alkyl)₂ and -NY'(C₁-C₈alkyl) wherein Y' is hydrogen or a group of the formula

In the compound 85, the end group bonded to the 2,2,6,6-tetramethylpiperidin-4-ylamino residue can be, for example, hydrogen and the end group bonded to the

In the compound 86, the end group bonded to the -O- can be, for example, hydrogen or

example, -OCH₃ or Cl.

In the compound 88, the end group bonded to the -O- can be, for example, hydrogen or

example, -OCH₃ or Cl.

In the compound 89, the end group bonded to the -CH₂- can be, for example, hydrogen and the end group bonded to the ester residue can be, for example,

In the compound 90, the end group bonded to the - CH_{2^-} can be, for example, hydrogen and the end group bonded to the ester residue can be, for example,

In the compound 91, the end group bonded to the - CH_2 - can be, for example, hydrogen and the end group bonded to the amide residue can be, for example,

In the compound 92, the end group bonded to the triazine residue can be, for example, chlorine or a group

and the end group bonded to the diamino residue can be, for example, hydrogen or a group

It may be convenient to replace the chlorine attached to the triazine by e.g. -OH or an amino group. Suitable amino groups are typically: pyrrolidin-1-yl, morpholino, -NH₂, -N(C₁-C₈alkyl)₂ and -NY'(C₁-C₈alkyl) wherein Y' is hydrogen or a group of the formula

Preferred is also a compound which corresponds to compound 92 wherein the 2,2,6,6-tetramethyl-4-piperidyl groups are replaced by 1,2,2,6,6-pentamethyl-4-piperidyl groups.

In the compound 93, the end group bonded to the diamino residue can be, for example, hydrogen and the end group bonded to the -CH₂CH₂- residue can be, for example,

In the compound 94, the end group bonded to the diamino residue can be, for example, hydrogen and the end group bonded to the diacyl residue can be, for example, Cl.

95)
$$-\frac{R''}{N-(CH_2)_2-N-(CH_2)_2} \frac{R''}{m'_{15}}$$

in which R" is a group of the formula

R" is a group of the formula (95-I), and

 m'_{15} and m''_{15} are each a number from 0 to 200, preferably 0 to 100, in particular 0 to 50, with the proviso that $m'_{15} + m''_{15}$ is a number from 2 to 200, preferably 2 to 100, in particular 2 to 50. In the compound 95, the end group bonded to the diamino residue can be, for example,

hydrogen and the end group bonded to the -CH₂CH₂- group can be, for example, halogen, in particular CI or Br.

Further examples for polymeric compounds are:

1) A compound of the formula (96-I) or (96-II)

wherein m_{16} and m_{16} are a number from 2 to 50, for example 2 to 25.

During the preparation, the compounds of the formulae (96-I) and (96-II) can be obtained together as a mixture and therefore, can also be employed as such. The (96-I):(96-II) weight ratio is, for example, from 20:1 to 1:20 or from 1:10 to 10:1.

In the compounds of the formula (96-I), the terminal group bonded to the nitrogen can be, for example, hydrogen and the terminal group bonded to the 2-hydroxypropylene radical can be, for example, a

group.

In the compounds of the formula (96-II), the terminal group bonded to the dimethylene radical can be, for example, -OH, and the terminal group bonded to the oxygen can be, for example, hydrogen. The terminal groups can also be polyether radicals.

2) A compound of the formula (97)

wherein G_{24} , G_{25} , G_{26} , G_{27} and G_{28} , independently of one another, are a direct bond or C_1 - C_{10} alkylene, G_{11} is as defined under (a') and m_{17} is a number from 1 to 50, for example 2 to 25.

In the compound of the formula (97), the end group bonded to the >C=O group can be, for example,

and the end group bonded to the oxygen can be, for example

Preferred are the following two compounds:

and

wherein the mean value of m_{17} is 2.5.

3) A compound of the formula (98)

in which approximately one third of the radicals R^{IV} are -C_2H_5 and the others are a group

and m_{18} is a number in the range from 2 to 200, preferably 2 to 100, in particular 2 to 50.

In the compound (98), the end group bonded to the -CH₂- residue can be, for example, hydrogen and the end group bonded to the -CH(CO₂R^N)- residue can be, for example, -CH=CH-COOR^N.

4) A compound of the formula (99)

in which G_{11} is as defined under (a'), G_{29} and G_{32} , independently of one another, are a direct bond or a -N(X₁)-CO-X₂-CO-N(X₃)- group, where X₁ and X₃, independently of one another, are hydrogen, C_1 - C_8 alkyl, C_5 - C_{12} cycloalkyl, phenyl, C_7 - C_8 phenylalkyl or a group of the formula (99-1)

$$\begin{array}{c}
CH_3 \\
CH_3
\end{array}$$

$$N-G_{11}$$

$$CH_3$$

$$CH_3$$

and X_2 is a direct bond or C_1 - C_4 alkylene, G_{30} , G_{31} , G_{34} and G_{35} , independently of one another, are hydrogen, C_1 - C_{30} alkyl, C_5 - C_{12} cycloalkyl or phenyl, G_{33} is hydrogen, C_1 - C_{30} alkyl, C_5 - C_{12} cycloalkyl, C_7 - C_9 phenylalkyl, phenyl or a group of the formula (99-1), and m_{19} is a number from 1 to 50.

In the compounds of the formula (99), the end group bonded to the 2,5-dioxopyrrolidine ring can be, for example, hydrogen, and the end group bonded to the $-C(G_{34})(G_{35})$ - radical can be, for example,

Examples of the compounds of the formula (99) are:

wherein G₁₁ is hydrogen or methyl, and m₁₉ is a number from 1 to 25.

5) A product obtainable by reacting an intermediate product, obtained by reaction of a polyamine of the formula (100a) with cyanuric chloride, with a compound of the formula (100b)

$$H_2N - (CH_2)_{\overline{m'_{20}}} NH - (CH_2)_{\overline{m''_{20}}} NH - (CH_2)_{\overline{m''_{20}}} NH_2$$
 (100a)

 $H - N - G_{3e}$ (100b)

 $H_3C - CH_3$
 G_{11}

in which m'₂₀, m"₂₀ and m"'₂₀, independently of one another, are a number from 2 to 12, G₃₆ is hydrogen, C₁-C₁₂alkyl, C₅-C₁₂cycloalkyl, phenyl or C₇-C₈phenylalkyl, and G₁₁ is as defined under (a'). A preferred product has the Chemical Abstracts-CAS No.

136 504-96-6 (Compound 100-A).

In general, the above reaction product can be represented for example by a compound of the formula 100-1, 100-2 or 100-3. It can also be in the form of a mixture of these three compounds.

A preferred meaning of the formula (100-1) is

A preferred meaning of the formula (100-2) is

A preferred meaning of the formula (100-3) is

In the above formulae 100-1 to 100-3, m_{20} is preferably 1 to 20.

6) A compound of the formula (101)

in which G_{11} is as defined under (a'), G_{37} is C_1 - C_{10} alkyl, C_5 - C_{12} cycloalkyl, C_1 - C_4 alkyl-substituted C_5 - C_{12} cycloalkyl, phenyl or C_1 - C_{10} alkyl-substituted phenyl, G_{38} is C_3 - C_{10} alkylene and m_{21} is a number from 1 to 50, for example 2 to 25.

In the compounds of the formula (101), the terminal group bonded to the silicon atom can be, for example, $(G_{37})_3$ Si-O-, and the terminal group bonded to the oxygen can be, for example, $-\text{Si}(G_{37})_3$.

The compounds of the formula (101) can also be in the form of cyclic compounds if m_{21} is a number from 3 to 10, i.e. the free valences shown in the structural formula then form a direct bond.

An example of a compound of the formula (101) is

13

with m₂₁ being a number from 1 to 20.

In the above shown oligomeric and polymeric compounds, examples of alkyl are methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, elcosyl and docosyl; examples of cycloalkyl are cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl; an example of C₇-C₉phenylalkyl is benzyl; and examples of alkylene are ethylene, propylene, trimethylene, tetramethylene, pentamethylene, 2,2-dimethyltrimethylene, hexamethylene, trimethylene, octamethylene and decamethylene.

(h') A compound of the formula (lh)

$$\begin{bmatrix}
G - CH_2 & CH_3 & O \\
G_{11} & N & N & G_{14}
\end{bmatrix}$$

$$G - CH_2 & CH_3 & O \\
G - CH_2 & CH_3 & O \\
G - CH_3 & O & O \\
G - CH_$$

in which n_6 is the number 1 or 2, G and G_{11} are as defined under (a'), and G_{14} is as defined under (b'), but G_{14} cannot be -CONH-Z and -CH₂-CH(OH)-CH₂-O-D-O-.

Examples of such compounds are the following:

(i') A compound of the formula (ii)

$$G_{39} \bigvee_{G_{39}} N \bigvee_{G_{39}} G_{39}$$
 (Ii)

wherein the radicals G₃₉, independently of one another, are a group of the formula (li-1)

in which G_{40} is C_1 - C_{12} alkyl or C_5 - C_{12} cycloalkyl, G_{41} is C_2 - C_{12} alkylene and G_{42} is hydrogen, C_1 - C_8 alkyl, -O', -CH₂CN, C_3 - C_6 alkenyl, C_7 - C_9 phenylalkyl, C_7 - C_9 phenylalkyl which is substituted on the phenyl radical by C_1 - C_4 alkyl; or C_1 - C_8 acyl.

Alkyl is for example C1-C4alkyl, in particular methyl, ethyl, propyl or butyl.

Cycloalkyl is preferably cyclohexyl.

Alkylene is for example ethylene, propylene, trimethylene, tetramethylene, pentamethylene, 2,2-dimethyltrimethylene or hexamethylene.

Alkenyl is preferably allyl.

Phenylalkyl is preferably benzyl.

Acyl is preferably acetyl.

Examples of compounds from this class are the compounds of the following formulae:

The sterically hindered amine (component (A)) is preferably one of the above compounds 1 to 106. The compounds 5, 10, 13, 14, 24, 25, 36-a, 36-b, 49-a-I, 49-a-II, 49-e, 63, 75, 76, 80-a, 81, 84-1, 84-2, 92, 93, 96-I, 96-II, 97-I, 97-II, 99-I, 100-A, 101-I, 105 and 106 are of interest. The compounds 5, 10, 13, 14, 36-a, 36-b, 36-d, 49-a-I, 49-a-II, 49-d, 49-e, 63, 69-a, 76, 80-a, 81, 84-1, 84-2, 92, 96-I, 96-II, 97-II, 99-II, 99-III, 100-A, 101-I and 105 are preferred and the compounds 13, 14, 36-a, 36-b, 49-a-I, 49-a-II, 63, 76, 81, 84-1, 92, 96-I, 96-II, 100-A and 101-I are particularly preferred.

The organic salt of zinc or magnesium defined in component (B) is preferably a compound of the formula MeL₂ in which Me is zinc or magnesium and L is an anion of an organic acid or of an enol. The organic acid can, for example, be a sulfonic acid, sulfinic acid, phosphonic acid or phosphinic acid, but is preferably a carboxylic acid. The acid can be aliphatic, aromatic, araliphatic or cycloaliphatic; it can be linear or branched; it can be substituted by hydroxyl or alkoxy groups; it can be saturated or unsaturated and it preferably contains 1 to 24 carbon atoms.

Examples of carboxylic acids of this type are formic, acetic, propionic, butyric, isobutyric, caprioic, 2-ethylcaproic, caprylic, capric, lauric, palmitic, stearic, behenic, oleic, lactic,

ricinoleic, 2-ethoxyproplonic, benzoic, salicylic, 4-butylbenzoic, toluic, 4-dodecylbenzoic, phenylacetic, naphthylacetic, cyclohexanecarboxylic, 4-butylcyclohexanecarboxylic or cyclohexylacetic acid. The carboxylic acid can also be a technical mixture of carboxylic acids, for example technical mixtures of fatty acids or mixtures of alkylated benzoic acids.

Examples of organic acids containing sulfur or phosphorus are methanesulfonic, ethanesulfonic, α,α -dimethylethanesulfonic, n-butanesulfonic, n-dodecanesulfonic, benzenesulfonic, toluenesulfonic, 4-nonylbenzenesulfonic, 4-dodecylbenzenesulfonic or cyclohexanesulfonic acid, dodecanesulfinic, benzenesulfinic or naphthalenesulfinic acid, butylphosphonic acid, phenylphosphonic acid, monomethyl or monoethyl phenylphosphonate, monobutyl benzylphosphonate, dibutylphosphinic acid or diphenylphosphinic acid.

If L is an enolate anion, it is preferably an anion of a β -dicarbonyl compound or of an o-acylphenol. Examples of β -dicarbonyl compounds are acetylacetone, benzoylacetone, dibenzoylmethane, ethyl acetoacetate, butyl acetoacetate, lauryl acetoacetate or α -acetylcyclohexanone. Examples of o-acylphenols are 2-acetylphenol, 2-butyroylphenol, 2-acetyl-1-naphthol, 2-benzoylphenol or salicylaldehyde. The enolate is preferably the anion of a β -dicarbonyl compound having 5 to 20 carbon atoms.

Organic salts of zinc or magnesium are preferably an acetylacetonate or an aliphatic monocarboxylate having, for example, 1 to 24 carbon atoms. Magnesium acetate, laurate and stearate, zinc formate, acetate, cenanthate, laurate and stearate as well as zinc acetylacetonate and magnesium acetylacetonate are some of the particular preferred examples.

Zinc stearate, magnesium stearate, zinc acetylacetonate, magnesium acetylacetonate, zinc acetate and magnesium acetate are of special interest.

The inorganic salt of zinc or magnesium is for example zinc oxide, magnesium oxide, zinc hydroxide, magnesium hydroxide, or a carbonate containing compound such as

 Zn-hydroxide-carbonate, Mg-hydroxide-carbonate, dolomite, e.g a Ca/Mg carbonate such as [®]Microdol Super from [®]Micro Minerals; or • a natural or synthetic hydrotalcite.

The natural hydrotalcite is held to possess a structure $Mg_6Al_2(OH)_{16}CO_3 \cdot 4 H_2O$. A typical empirical formula of a synthetic hydrotalcite is

Al₂Mg_{4.35}OH_{11.36}CO_{3(1.67)} • x H₂O.

Examples of the synthetic product include:

 $Mg_{0.7}Al_{0.3}(OH)_2(CO_3)_{0.15} \cdot 0.54 H_2O$,

Mg_{4.5}Al₂(OH)₁₃CO₃ · 3.5 H₂O, or

Mg_{4,2}AI(OH)_{12,4}CO₃.

: :

Preferred synthetic hydrotalcites are L-55R[®]II from [®]REHEIS as well as [®]ZHT-4A and [®]DHT-4A from [®]Kyowa Chemical Industry Co.

The two different compounds of component (B), which are present in a weight ratio of 1:10 to 10:1 are for example:

- Mg-stearate and hydrotalcite (*DHT-4A),
- Zn-stearate and hydrotalcite (*DHT-4A),
- Mg-acetylacetonate and hydrotalcite (*DHT-4A),
- Mg-oxide and hydrotalcite (*DHT-4A),
- Mg-hydroxide and hydrotalcite (*DHT-4A).
- Zn-hydroxide-carbonate and Mg-stearate,
- Zn-hydroxide-carbonate and Zn-stearate,
- Zn-hydroxide-carbonate and Mg-acetylacetonate,
- Zn-hydroxide-carbonate and Mg-oxide,
- Zn-hydroxide-carbonate and Zn-oxide,
- Zn-hydroxide-carbonate and Mg-hydroxide,
- hydrotalcite (PREHEIS) and Mg-stearate,
- hydrotalcite (*REHEIS) and Zn-stearate,
- hydrotalcite (*REHEIS) and Mg-oxide,
- dolomite ([®]Microdol Super) and Zn-stearate,
- dolomite (*Microdol Super) and Mg-stearate,
- dolomite (*Microdol Super) and Zn-oxide,

- dolomite ([®]Microdol Super) and Mg-hydroxide,
- Mg-stearate and Zn-stearate,
- Mg-stearate and Zn-acetylacetonate,
- Mg-stearate and Mg-oxide,
- Mg-stearate and Zn-oxide,
- Mg-stearate and Mg-hydroxide,
- Zn-stearate and Mg-acetate,
- Zn-stearate and Mg-oxide,
- Zn-stearate and Mg-hydroxide,
- Mg-acetylacetonate and Zn-acetylacetonate,
- Mg-acetylacetonate and Mg-oxide,
- Mg-acetylacetonate and Zn-oxide,
- Mg-acetylacetonate and Mg-hydroxide,
- Zn-acetylacetonate and Mg-oxide,
- Zn-acetylacetonate and Zn-oxide, or
- Mg-oxide and Zn-oxide.

A preferred embodiment of this invention relates to a stabilizer mixture wherein the two different compounds of component (B) are selected from the group consisting of hydrotalcite, dolomite, Zn-hydroxide-carbonate, Mg-hydroxide-carbonate, Zn-oxide, Mg-oxide, Zn-hydroxide, Mg-hydroxide, Zn-stearate, Mg-stearate, Zn-acetylacetonate, Mg-acetylacetonate, Zn-acetate and Mg-acetate.

According to a particular preferred embodiment component (B) does not contain Zn-oxide.

A stabilizer mixture wherein the two different compounds in component (B) are

- Mg-stearate and hydrotalcite,
- Zn-stearate and hydrotalcite,
- Mg-stearate and Zn-stearate,
- Zn-stearate and Mg-oxide, or
- Mg-stearate and Mg-hydroxide is also preferred.

A further preferred embodiment of this invention relates to a stabilizer mixture containing additionally

- (C1) a pigment or
- (C2) an UV absorber or
- (C3) a pigment and an UV absorber.

The pigment (component (C1)) may be an inorganic or organic pigment.

Examples of inorganic pigments are titanium dioxide, zinc oxide, carbon black, cadmium sulfide, cadmium selenide, chromlum oxide, iron oxide, lead oxide and so on.

Examples of organic pigments are azo pigments, anthraquinones, phthalocyanines, tetrachloroisoindolinones, quinacridones, isoindolines, perylenes, pyrrolopyrroles (such as Pigment Red 254) and so on.

All pigments described in "Gächter/Müller: Plastics Additives Handbook, 3rd Edition, Hanser Publishers, Munich Vienna New York", page 647 to 659, point 11.2.1.1 to 11.2.4.2 can be used as component (C1).

A particularly preferred pigment is titanium dioxide, optionally in combination with an organic pigment.

Examples of such organic pigments are:

C.I. (Colour Index) Pigment Yellow 93, C.I. Pigment Yellow 95, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 155, C.I. Pigment Yellow 162, C.I. Pigment Yellow 168, C.I. Pigment Yellow 180, C.I. Pigment Yellow 183, C.I. Pigment Red 44, C.I. Pigment Red 170, C.I. Pigment Red 202, C.I. Pigment Red 214, C.I. Pigment Red 254, C.I. Pigment Red 264, C.I. Pigment Red 272, C.I. Pigment Red 48:2, C.I. Pigment Red 48:3, C.I. Pigment Red 53:1, C.I. Pigment Red 57:1, C.I. Pigment Green 7, C.I. Pigment Blue 15:1, C.I. Pigment Blue 15:3 and C.I. Pigment Violet 19.

Examples of the UV absorber (component (C2)) are a 2-(2'-hydroxyphenyl)benzotriazole, a 2-hydroxybenzophenone, an ester of substituted or unsubstituted benzoic acid, an acrylate,

an oxamide, a 2-(2-hydroxyphenyl)-1,3,5-triazine, a monobenzoate of resorcinol or a formamidine.

The 2-(2'-hydroxyphenyl)benzotriazole is e.g. 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl- 2'-hydroxy-5'-methylphenyl)-5chloro-benzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis-(α , α -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, mixture of 2-(3'-tert-butyl-2'hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-5'-[2-(2ethylhexyloxy)-carbonylethyl]-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2octyloxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenylbenzotriazole, 2,2'-methylene-bis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-ylphenol] or the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300; [R-CH2CH2-COO(CH2)3-]2 where R = 3'-tert-butyl-4'hydroxy-5'-2H-benzotriazol-2-ylphenyl.

2-(3',5'-Di-tert-butyl-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chloro-benzotriazole and 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)-benzotriazole are preferred.

The 2-hydroxybenzophenone is for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy or 2'-hydroxy-4,4'-dimethoxy derivatives.

2-Hydroxy-4-octyloxybenzophenone is preferred.

The ester of a substituted or unsubstituted benzolc acid is for example 4-tert-butyl-phenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl) resorcinol, benzoyl resorcinol, 2,4-di-tertbutylphenyl 3,5-di-tert-butyl-4-hydroxybenzo-

ate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate or 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2,4-Di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate and hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate are preferred.

The acrylate is for example ethyl α -cyano- β , β -diphenylacrylate, isooctyl α -cyano- β , β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl-p-methoxycinnamate, butyl α -cyano- β -methyl-p-methoxy-cinnamate, methyl α -carbomethoxy-p-methoxycinnamate or N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

The oxamide is for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-diodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide or its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide or mixtures of ortho- and para-methoxy-disubstituted oxanilides or mixtures of o- and p-ethoxy-disubstituted oxanilides.

The 2-(2-hydroxyphenyl)-1,3,5-triazine is for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxyphenyl)-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-4-(2-hydroxy-3-dodecyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine.

2-(2-Hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine and 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine are preferred.

The monobenzoate of resorcinol is for example the compound of the formula

The formamidine is for example the compound of the formula

$$H_{\xi}C_{2}O$$
 C
 N
 $C_{\xi}H_{\xi}$

The UV absorber is in particular a

2-(2'-hydroxyphenyl)benzotriazole, a 2-hydroxybenzophenone or a hydroxyphenyltriazine.

A further preferred embodiment of this invention relates to a stabilizer mixture containing additionally an organic salt of Ca or an Inorganic salt of Ca.

Examples of an organic salt of Ca are Ca-stearate, Ca-laurate, Ca-lactate and Ca-stearoyllactate.

Examples of an inorganic salt of Ca are CaO and Ca(OH)2.

The stabilizer mixture according to this invention is suitable for stabilizing organic materials against degradation induced by light, heat or oxidation. Examples of such organic materials are the following:

1. Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-1-ene, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbomene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight poly-

ethylene (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), (VLDPE) and (ULDPE).

Polyolefins, i.e. the polymers of monoolefins exemplified in the preceding paragraph, preferably polyethylene and polypropylene, can be prepared by different, and especially by the following, methods:

- a) radical polymerisation (normally under high pressure and at elevated temperature).
- b) catalytic polymerisation using a catalyst that normally contains one or more than one metal of groups IVb, Vb, Vlb or VIII of the Periodic Table. These metals usually have one or more than one ligand, typically oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls that may be either π- or σ-coordinated. These metal complexes may be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium(III) chloride, alumina or silicon oxide. These catalysts may be soluble or insoluble in the polymerisation medium. The catalysts can be used by themselves in the polymerisation or further activators may be used, typically metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyloxanes, said metals being elements of groups Ia, Ila and/or Illa of the Periodic Table. The activators may be modified conveniently with further ester, ether, amine or silyl ether groups. These catalyst systems are usually termed Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC).
- 2. Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).
- 3. Copolymers of monoolefins and diolefins with each other or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, propylene/isobutylene copolymers, ethylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/octene

lene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers and their copolymers with carbon monoxide or ethylene/acrylic acid copolymers and their salts (ionomers) as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylidene-norbomene; and mixtures of such copolymers with one another and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LLDPE/EVA, LLDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.

- 4. Hydrocarbon resins (for example C_5 - C_9) including hydrogenated modifications thereof (e.g. tackifiers) and mixtures of polyalkylenes and starch.
- 5. Polystyrene, poly(p-methylstyrene), poly(α -methylstyrene).
- 6. Copolymers of styrene or α-methylstyrene with dienes or acrylic derivatives, for example styrene/butadiene, styrene/acrylonitrile, styrene/alkyl methacrylate, styrene/butadiene/alkyl acrylate, styrene/butadiene/alkyl methacrylate, styrene/maleic anhydride, styrene/acrylonitrile/methyl acrylate; mixtures of high impact strength of styrene copolymers and another polymer, for example a polyacrylate, a diene polymer or an ethylene/propylene/diene terpolymer; and block copolymers of styrene such as styrene/butadiene/styrene, styrene/isoprene/styrene, styrene/ethylene/butylene/styrene or styrene/ethylene/propylene/ styrene.
- 7. Graft copolymers of styrene or α-methylstyrene, for example styrene on polybutadiene, styrene on polybutadiene-styrene or polybutadiene-acrylonitrile copolymers; styrene and acrylonitrile (or methacrylonitrile) on polybutadiene; styrene, acrylonitrile and methyl methacrylate on polybutadiene; styrene and maleic anhydride on polybutadiene; styrene and maleimide on polybutadiene; styrene and maleimide on polybutadiene; styrene and alkyl acrylates or methacrylates on polybutadiene; styrene and acrylonitrile on ethylene/propylene/diene terpolymers; styrene and acrylonitrile on polyalkyl acrylates or polyalkyl methacrylates, styrene and acrylonitrile on acrylate/butadiene copolymers, as well as mixtures thereof with the copolymers listed under 6), for example the copolymer mixtures known as ABS, MBS, ASA or AES polymers.

- 8. Halogen-containing polymers such as polychloroprene, chlorinated rubbers, chlorinated and brominated copolymer of isobutylene-isoprene (halobutyl rubber), chlorinated or sulfo-chlorinated polyethylene, copolymers of ethylene and chlorinated ethylene, epichlorohydrin homo- and copolymers, especially polymers of halogen-containing vinyl compounds, for example polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polyvinylidene fluoride, as well as copolymers thereof such as vinyl chloride/vinylidene chloride, vinyl chloride/vinyl acetate or vinylidene chloride/vinyl acetate copolymers.
- 9. Polymers derived from α,β -unsaturated acids and derivatives thereof such as polyacrylates and polymethacrylates; polymethyl methacrylates, polyacrylamides and polyacrylonitriles, impact-modified with butyl acrylate.
- 10. Copolymers of the monomers mentioned under 9) with each other or with other unsaturated monomers, for example acrylonitrile/ butadiene copolymers, acrylonitrile/alkyl acrylate copolymers, acrylonitrile/alkoxyalkyl acrylate or acrylonitrile/vinyl halide copolymers or acrylonitrile/ alkyl methacrylate/butadiene terpolymers.
- 11. Polymers derived from unsaturated alcohols and amines or the acyl derivatives or acetals thereof, for example polyvinyl alcohol, polyvinyl acetate, polyvinyl stearate, polyvinyl benzoate, polyvinyl maleate, polyvinyl butyral, polyallyl phthalate or polyallyl melamine; as well as their copolymers with olefins mentioned in 1) above.
- 12. Homopolymers and copolymers of cyclic ethers such as polyalkylene glycols, polyethylene oxide, polypropylene oxide or copolymers thereof with bisglycidyl ethers.
- 13. Polyacetals such as polyoxymethylene and those polyoxymethylenes which contain ethylene oxide as a comonomer; polyacetals modified with thermoplastic polyurethanes, acrylates or MBS.

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14. Polyphenylene oxides and sulfides, and mixtures of polyphenylene oxides with styrene polymers or polyamides.

- 15. Polyurethanes derived from hydroxyl-terminated polyethers, polyesters or polybutadienes on the one hand and aliphatic or aromatic polyisocyanates on the other, as well as precursors thereof.
- 16. Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, for example polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12, 4/6, 12/12, polyamide 11, polyamide 12, aromatic polyamides starting from m-xylene diamine and adipic acid; polyamides prepared from hexamethylenediamine and isophthalic or/and terephthalic acid and with or without an elastomer as modifier, for example poly-2,4,4,-trimethylhexamethylene terephthalamide or poly-m-phenylene isophthalamide; and also block copolymers of the aforementioned polyamides with polyolefins, olefin copolymers, ionomers or chemically bonded or grafted elastomers; or with polyethers, e.g. with polyethylene glycol, polypropylene glycol or polytetramethylene glycol; as well as polyamides or copolyamides modified with EPDM or ABS; and polyamides condensed during processing (RIM polyamide systems).
- 17. Polyureas, polyimides, polyamide-imides, polyetherimids, polyesterimids, polyhydantoins and polybenzimidazoles.
- 18. Polyesters derived from dicarboxylic acids and diols and/or from hydroxycarboxylic acids or the corresponding lactones, for example polyethylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylolcyclohexane terephthalate and polyhydroxybenzoates, as well as block copolyether esters derived from hydroxyl-terminated polyethers; and also polyesters modified with polycarbonates or MBS.
- 19. Polycarbonates and polyester carbonates.
- 20. Polysulfones, polyether sulfones and polyether ketones.
- 21. Crosslinked polymers derived from aldehydes on the one hand and phenois, ureas and melamines on the other hand, such as phenol/formaldehyde resins, urea/formaldehyde resins and melamine/formaldehyde resins.
- 22. Drying and non-drying alkyd resins.

- 23. Unsaturated polyester resins derived from copolyesters of saturated and unsaturated dicarboxylic acids with polyhydric alcohols and vinyl compounds as crosslinking agents, and also halogen-containing modifications thereof of low flammability.
- 24. Crosslinkable acrylic resins derived from substituted acrylates, for example epoxy acrylates, urethane acrylates or polyester acrylates.
- 25. Alkyd resins, polyester resins and acrylate resins crosslinked with melamine resins, urea resins, isocyanates, isocyanates, polyisocyanates or epoxy resins.
- 26. Crosslinked epoxy resins derived from aliphatic, cycloaliphatic, heterocyclic or aromatic glycidyl compounds, e.g. products of diglycidyl ethers of bisphenol A and bisphenol F, which are crosslinked with customary hardeners such as anhydrides or amlnes, with or without accelerators.
- 27. Natural polymers such as cellulose, rubber, gelatin and chemically modified homologous derivatives thereof, for example cellulose acetates, cellulose propionates and cellulose butyrates, or the cellulose ethers such as methyl cellulose; as well as rosins and their derivatives.
- 28. Blends of the aforementioned polymers (polyblends), for example PP/EPDM, Polyamide/EPDM or ABS, PVC/EVA, PVC/ABS, PVC/MBS, PC/ABS, PBTP/ABS, PC/ASA, PC/PBT, PVC/CPE, PVC/acrylates, POM/thermoplastic PUR, PC/thermoplastic PUR, POM/acrylate, POM/MBS, PPO/HIPS, PPO/PA 6.6 and copolymers, PA/HDPE, PA/PP, PA/PPO, PBT/PC/ABS or PBT/PET/PC.
- 29. Naturally occurring and synthetic organic materials which are pure monomeric compounds or mixtures of such compounds, for example mineral oils, animal and vegetable fats, oil and waxes, or oils, fats and waxes based on synthetic esters (e.g. phthalates, adipates, phosphates or trimellitates) and also mixtures of synthetic esters with mineral oils in any weight ratios, typically those used as spinning compositions, as well as aqueous emulsions of such materials.

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30. Aqueous emulsions of natural or synthetic rubber, e.g. natural latex or latices of carboxylated styrene/butadiene copolymers.

This invention therefore additionally relates to a composition comprising an organic material subject to degradation induced by light, heat or oxidation and the stabilizer mixture described above; with the proviso that the organic material is essentially free of perchloric acid.

A further embodiment of the present invention is a method for stabilizing an organic material against degradation induced by light, heat or oxidation, which comprises incorporating into the organic material the stabilizer mixture described above; with the proviso that the organic material is essentially free of perchloric acid.

The organic material is preferably a synthetic polymer, in particular from one of the above groups. Polyolefins are preferred and polyethylene, polypropylene and copolymers thereof are particularly preferred.

The components (A), (B) and optionally (C1) and/or (C2) may be added to the organic material to be stabilized either individually or mixed with one another.

The sterically hindered amine compound (component (A)) is present in the organic material in an amount of preferably 0.01 to 5 %, in particular 0.01 to 1 % or 0.05 to 1 %, relative to the weight of the organic material.

The two different Mg and/or Zn salts (component (B)), together, are present in the organic material in an amount of preferably 0.005 to 1 %, in particular 0.05 to 0.2 %, relative to the weight of the organic material.

The pigment (component (C1)) is optionally present in the organic material in an amount of preferably 0.01 to 10 %, in particular 0.05 to 1 %, relative to the weight of the organic material.

The UV absorber (component (C2)) is optionally present in the organic material in an amount of preferably 0.01 to 1 %, in particular 0.05 to 0.5 %, relative to the weight of the organic material.

The total amount of component (C3) (the pigment in combination with the UV absorber) is preferably 0.01 to 10 %, relative to the weight of the organic material. The weight ratio of the UV absorber to the pigment is for example 2:1 to 1:10.

When the pigment used is titanium dioxide in combination with an organic pigment as described above, titanium dioxide is preferably present in the organic material in an amount of 0.01 to 5 %, relative to the weight of the organic material, and the organic pigment may be present in an amount of, for example, 0.01 to 2 %, relative to the weight of the organic material.

The weight ratio of the components (A):(B) is preferably 10:1 to 1:10.

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The weight ratio of the components (A):(C1) is preferably 10:1 to 1:10.

The weight ratio of the components (A):(C2) is preferably 20:1 to 1:2.

The weight ratio of the components (A):(C3) is preferably 10:1 to 1:10.

The above components can be incorporated into the organic material to be stabilized by known methods, for example before or during shaping or by applying the dissolved or dispersed compounds to the organic material, if necessary with subsequent evaporation of the solvent. The components can be added to the organic material in the form of a powder, granules or a masterbatch, which contains these components in, for example, a concentration of from 2.5 to 25% by weight.

If desired, the components (A), (B) and optionally (C1) and/or (C2) can be melt blended with each other before incorporation in the organic material. They can be added to a polymer before or during the polymerization or before the crosslinking.

The materials stabilized according to this invention can be used in a wide variety of forms, for example as films, fibres, tapes, moulding compositions, profiles or as binders for paints, adhesives or putties.

The stabilized material may additionally also contain various conventional additives, for example:

1. Antioxidants

- 1.1. Alkvlated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butyl-phenol, 2,6-di-tert-butyl-4-lisobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α-methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tri-cyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example, 2,6-di-nonyl-4-methyl-phenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyl-heptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyl
- 1.2. Alkvithiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.
- 1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl) adipate.
- 1.4. Tocopherols, for example α-tocopherol, β-tocopherol, γ-tocopherol, δ-tocopherol and mixtures thereof (Vitamin E).
- 1.5. Hydroxylated thlodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis-(3,6-di-sec-amylphenol), 4,4'-bis-(2,6-dimethyl-4-hydroxyphenyl) disulfide.

- 1.6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tertbutylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tertbutyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'methylenebis[6-(α , α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tertbutylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5tert-butyi-4-hydroxy-2-methyl-phenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5methyl-phenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tertbutyl-4-hydroxy2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tertbutyl-4-hydroxy2-methylphenyl)pentane.
- 1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5di-tert-butyl-4-hydroxybenzylmercaptoacetate.
- 1.8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis-(3,5-di-tert-butyl-2-hydroxybenzyl)-malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-dodecylmercaptoethyl-2,2-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.
- 1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-

hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

- 1.10. Triazine Compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxyphenzyl)isocyanurate.
- 1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.
- 1.12. Acylaminophenois, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.
- 1.13. Esters of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris-(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.
- 1.14. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with monoor polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol,

pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

- 1.15. Esters of β-(3.5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris-(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.
- 1.16. Esters of 3.5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris-(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxablcyclo[2.2.2]octane.
- 1.17. Amides of β -(3.5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine.

1.18. Ascorbic acid (vitamin C)

1.19. Aminic antioxidants, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-(1-meth

cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfamoyl)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylamino-phenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, Bis[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines, a mixture of mono- und dialkylated tert-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- und dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- und dialkylated tert-octyl-phenothiazines, N-allylphenothiazin, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethyl-piperid-4-yl-hexamethylenediamine, bis(2,2,6,6-tetramethylpiperid-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

2. UV absorbers and light stabilisers

Nickel compounds, for example nickel complexes of 2,2'-thio-bis-[4-(1,1,3,3-tetra-methylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphenyl undecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

- 3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl) hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxy-phenylpropionyl) hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)-oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenyl-hydrazide, N,N'-diacetyladipoyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.
- 4. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, triauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-ditert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)-pentaerythritol diphosphite, diisodecyloxypentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl)pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocin, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphosphite, bis(2,4-di-tert-butyl-6-methylphosphite)
- 5. Hydroxylamines, for example, N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

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6. Nitrones, for example, N-benzyl-alpha-phenyl-nitrone, N-ethyl-alpha-methyl-nitrone, N-octyl-alpha-heptyl-nitrone, N-lauryl-alpha-undecyl-nitrone, N-tetradecyl-alpha-tridecyl-nitrone, N-hexadecyl-alpha-pentadecyl-nitrone, N-octadecyl-alpha-heptadecyl-nitrone, N-octadecyl-alpha-pentadecyl-nitrone, N-hexadecyl-alpha-heptadecyl-nitrone, N-octadecyl-alpha-heptadecyl-nitrone, N-octadecyl-alpha-hexadecyl-nitrone, nitrone derived from N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

- 7. Thiosynergists, for example, dilauryl thiodipropionate or distearyl thiodipropionate.
- 8. Peroxide scavengers, for example esters of β -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis(β -dodecylmercapto)propionate.
- 9. Basic co-stabilisers, for example, melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or tin pyrocatecholate.
- 10. Nucleating agents, for example, inorganic substances such as talcum, metal oxides such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, alkaline earth metals; organic compounds such as monoor polycarboxylic acids and the salts thereof, e.g. 4-tert-butylbenzolc acid, adipic acid, diphenylacetic acid, sodium succinate or sodium benzoate; polymeric compounds such as ionic copolymers ("ionomers").
- 11. Fillers and reinforcing agents, for example, calcium carbonate, sllicates, glass fibres, glass bulbs, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood flour and flours or fibers of other natural products, synthetic fibers.
- 12. Other additives, for example, plasticisers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing agents, antistatic agents and blowing agents.

13. Benzofuranones and indolinones, for example those disclosed in US-A-4325863, US-A-4338244, US-A-5175312, US-A-5216052, US-A-5252643, DE-A-4316611, DE-A-4316622, DE-A-4316876, EP-A-0589839 or EP-A-0591102 or 3-[4-(2-acetoxyethoxy)phenyl]-5,7-di-tert-butyl-benzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butyl-benzofuran-2-one.

Particularly preferred conventional additives are those listed above under items 1 and/or 4.

Also the compound of the formula

is one of the preferred conventional additives which may additionally be incorporated into the organic material to be stabilized.

The weight ratio of the total amount of components (A), (B) and optionally (C1) and/or (C2) to the total amount of the conventional additives can be, for example, 100:1 to 1:100.

The examples below illustrate the invention in greater detail. All percentages and parts are by weight, unless stated otherwise.

Sterically hindered amine compounds used in the following Examples I to VII: (For the polymeric compounds, the mean degree of polymerization is indicated in each case.)

Compound 5:

(Dastib 845)

Compound 10:

(Tinuvin 780)

Compound 13:

(*Tinuvin 770)

Compound 14:

(*Tinuvin 765)

Compound 36-a:

([®]Mark LA57)

Compound 36-b:

(Mark LA52)

Compound 36-d:

(*Sanduvor PR-31)

Compound 49-a-l:

(*HALS S95)

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Compound 49-a-II:

(*HALS Methyl S95)

Compound 49-d:

(*Uvinul 4050 H)

Compound 49-e:

(*Diacetam 5)

Compound 63:

(*Hostavin N20)

Compound 69-a:

(*Sanduvor 3050)

Compound 76:

(*Chimassorb 119)

Compound 80-a;

(*Uvinul 4049)

Compound 81:

(*Tinuvin 622)

with m₁ being 5.1.

Compound 84-1:

(*Chimassorb 944)

with m₄ being 4.5.

Compound 84-2:

(*Dastib1082)

with m₄ being 4.3.

Compound 92:

(*Cyasorb UV 3346)

with m₄ being 3.5.

Mixture of the compounds 96-I and 96-II:

(Preferably ^eHostavin N30)

with m_{16} being 3.9 and m_{16} * being 4.2 and the weight ratio of (96-I) to (96-II) being 4:1.

Compound 97-II:

(Mark LA 63)

with m_{17} being 2.5.

Compound 99-I':

(*Uvinul 5050 H)

with m₁₉ being 3.2.

Compound 99-II':

(*Lichtschutzstoff UV 31)

with m₁₉ being 3.

Compound 99-III':

(*Luchem HA B18)

with m_{19} being a number from 1 to 25.

Compound 100-A:

(*Uvasorb HA88 (Chemical Abstracts CAS No. 136 504-96-6))

A product obtainable by reacting an intermediate product, obtained by reaction of a polyamine of the formula (100a-l) with cyanuric chloride, with a compound of the formula (100b-l).

$$H_2N - (CH_2)_3 - NH - (CH_2)_2 - NH - (CH_2)_3 - NH_2$$
 (100a-l)

 $H - N - C_4H_9 - n$ (100b-l)

 $H_3C - N - CH_3$
 $H_3C - N - CH_3$

Compound 101-I:

(Preferably [®]Uvasil 299)

with m₂₁ being 5.8.

Compound 105:

(*Goodrite UV 3150)

Example I: Light stabilization of injection molded 2 mm polypropylene plaques.

100 parts of polypropylene powder (melt flow index: 2.4 g/10 min at 230°C and 2160 g) are blended in a barrel mixer with 0.05 parts of pentaerythrityl tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.05 parts of tris[2,4-di-tert-butylphenyl] phosphite, and the stabilizer system indicated in Tables 1 to 4. Then, the blend is compounded in an extruder at temperatures of 200°-220 °C. The granules obtained on extrusion and granulation are transformed into 2 mm thick plaques at 240°-260°C in an automatic injection molding machine.

The plaques are mounted on sample holders and subjected to natural weathering in Florida (45° South, direct, approximately 140 kLy/year). Periodically, the carbonyl content of the samples is measured with an infrared spectrophotometer. The exposure time corresponding to formation of a carbonyl absorbance of, for example, 0.5 (T_{0.5}) is a measure for the efficiency of the stabilizer system.

The values obtained are summarized in Tables 1 to 4.

The synergistic effect of the two coadditivs ((1) and (2)) is determined by a comparison of the calculated T_{0.5} value with the actually measured T_{0.5} value. The T_{0.5} values are calculated on the basis of the additivity law (B. Ranby and J.F. Rabek; Photodegradation, Photo-oxidation and Photostabilization of Polymers, Principles and Applications, John Wiley & Sons, London, New York, Sydney, Toronto, 1975, pages 418 and 419) according to the following equation:

Expected stabilizing activity = Stabilizing activity of 100 % (1) + stabilizing activity of 100 % (2)

There is a synergistic effect for the two coadditivs in question, when $T_{0.5 \text{ measured}} > T_{0.5 \text{ calculated.}}$

Table 1:

Sterically hindered amine compound: 0.1 % of the compound 81

Coadditiv	T _{0.5 measured} (kLy)	T _{0.5 calcutated} (KLy)
0.1 % of hydrotalcite (*DHT-4A)	67	
0.1 % of Mg-hydroxide-carbonate	57	
0.1% of Zn-hydroxide-carbonate	81	
0.1 % of Mg-stearate	71	

0.1 % of Zn-stearate	72	
0.1 % of Mg-acetylacetonate	53	
0.1 % of Mg-oxide	94	
0.1 % of Zn-Oxide	73	
0.1 % of Mg-hydroxide	60	
0.1% of hydrotalcite (®REHEIS)	66	
0.1% of dolomite (*Microdol Super)	53	
0.05 % of Mg-stearate +	85	69
0.05 % of hydrotalcite (*DHT-4A)	<u>.</u>	••
0.05 % of Zn-stearate +	86	69.5
0.05 % of hydrotalcite ([®] DHT-4A)		
0.05 % of Mg-acetylacetonate +	92	60
0.05 % of hydrotalcite ([®] DHT-4A)	<u> </u>	
0.05 % of Zn-hydroxide-carbonate +	. 100	77.5
0.05 % of Mg-stearate	. 100	.,,,
0.05 % of Zn-hydroxide-carbonate +	124	76.5
0.05 % of Zn-stearate		
0.05 % of Zn-hydroxide-carbonate +	106	67.5
0.05 % of Mg-acetylacetonate		
0.05 % of Zn-hydroxide-carbonate +	111	87.5
0.05 % of Mg-oxide	1 '''	07.0
0.05 % of Zn-hydroxide-carbonate +	164	77
0.05 % of Zn-oxide	104	"
0.05 % of Zn-hydroxide-carbonate +	86	70.5
0.05 % of Mg-hydroxide	80	70.3
0.05 % of hydrotalcite (*REHEIS) +	104	68.5
0.05 % of Mg-stearate	104	00.5
0.05 % of hydrotalcite (*REHEIS) +	131	69
0.05 % of Zn-stearate	131	05
0.05 % of dolomite (*Microdol Super) +	78	62.5
0.05 % of Zn-stearate	/°	62.5
	<u> </u>	<u>L</u>

. .

0.05 % of dolomite (Microdol Super) +	00		
0.05 % of Mg-stearate	66	62	
0.05 % of dolomite (Microdol Super) +			
0.05 % of Zn-oxide	74	63	
0.05 % of dolornite (*Microdol Super) +			
95 % of Mg-hydroxide 60		56.5	

Table 2:
Sterically hindered amine compound: 0.1 % of the compound 84-1

Coadditiv	T _{0.2 measured} (kLy)	T _{0.2 calculated}
0.1 % of hydrotalcite (*DHT-4A)	144	
0.1 % of Mg-hydroxide-carbonate	124	
0.1 % of Zn-hydroxide-carbonate	136	
0.1 % of Mg-stearate	140	
0.1 % of Zn-stearate	164	
0.1 % of Mg-acetylacetonate	97	
0.1 % of Mg-oxide	171	
0.1 % of Zn-oxide	258	
0.1 % of Mg-hydroxide	165	
0.1 % of hydrotalcite (*REHEIS)	133	
0.1 % of dolomite (*Microdol Super)	80	
.05 % of Mg-stearate + .05 % of hydrotalcite (*DHT-4A)	174	142

0.05.0/ -4.744		
0.05 % of Zn-stearate +	232	154
0.05 % of hydrotalcite (*DHT-4A)		
0.05 % of Mg-acetylacetonate +	146	120.5
0.05 % of hydrotalcite (*DHT-4A)		
0.05 % of Mg-oxide +	210	157.5
0.05 % of hydrotalcite (®DHT-4A)		
0.05 % of Mg-hydroxide +	192	154.5
0.05 % of hydrotalcite (®DHT-4A)		
0.05 % of Zn-hydroxide-carbonate +	183	138
0.05 % of Mg-stearate		
0.05 % of Zn-hydroxide-carbonate +	154	150
0.05 % of Zn-stearate	104	150
0.05 % of Zn-hydroxide-carbonate +	151	116.5
0.05 % of Mg-acetylacetonate	131	110.5
0.05 % of Zn-hydroxide-carbonate +	204	153.5
0.05 % of Mg-oxide	204	135.5
0.05 % of Zn-hydroxide-carbonate +	266	197
0.05 % of Zn-oxide		
0.05 % of Zn-hydroxide-carbonate +	171	150.5
0.05 % of Mg-hydroxide		
0.05 % of hydrotalcite (*REHEIS) +	151	136.5
0.05 % of Mg-stearate		100.0
0.05 % of hydrotalcite (*REHEIS) +	177	148.5
0.05 % of Zn-stearate	···	1.0.0
0.05 % of hydrotalcite (*REHEIS) +	167	152
0.05 % of Mg-oxide	,	
0.05 % of dolomite (*Microdol Super) +	133	122
0.05 % of Zn-stearate	133	122
0.05 % of dolomite (*Microdol Super) +	190	169
0.05 % of Zn-oxide	190	109
		1

Table 3:

Sterically hindered amine compound:

UV absorber:

0.05 % of the compound 81

0.05 % of the compound of the formula

Coadditiv	T _{0.2 measured} (kLy)	T _{0.2} calculated (KLy)
0.1 % of hydrotalcite (*DHT-4A)	127	
0.1 % of Mg-hydroxide-carbonate	122	
0.1 % of Zn-hydroxide-carbonate	121	
0.1 % of Mg-stearate	216	
0.1 % of Zn-stearate	200	
0.1 % of Mg-acetylacetonate	202	
0.1 % of Mg-oxide	176	
0.1 % of Zn-oxide	70	
.1 % of Mg-hydroxide	146	
.1 % of hydrotalcite (*REHEIS)	144	
.1 % of dolomite (*Microdol Super)	77	
1 % of Mg-acetate	186	
1 % of Zn-acetylacetonate	68	
05 % of hydrotalcite (*DHT-4A) + 05 % of Mg-stearate	236	171.5
05 % of hydrotalcite (*DHT-4A) + 05 % of Zn-stearate	196	163.5

0.05 % of hydrotalcite (*DHT-4A) +	230	164.5
0.05 % of Mg-acetylacetonate		
0.05 % of hydrotalcite (*DHT-4A) +	165	151.5
0.05 % of Mg-oxide		
0.05 % of Zn-hydroxide-carbonate +	224	168.5
0.05 % of Mg-stearate		·
0.05 % of Zn-hydroxide-carbonate +	248	161.5
0.05 % of Mg-acetylacetonate		
0.05 % of Zn-hydroxide-carbonate +	184	148.5
0.05 % of Mg-oxide		
0.05 % of Zn-hydroxide-carbonate +	144	95.5
0.05 % of Zn-oxide		
0.05 % of Zn-hydroxide-carbonate +	165	133.5
0.05 % of Mg-hydroxide		
0.05 % of hydrotalcite (*REHEIS) +	304	180
0.05 % of Mg-stearate		
0.05 % of hydrotalcite (*REHEIS) +	288	172
0.05 % of Zn-stearate		
0.05 % of dolomite (Microdol Super) +	192	146.5
0.05 % of Mg-stearate		
0.05 % of dolornite (Microdol Super) +	. 172	138.5
0.05 % of Zn-stearate		
0.05 % of Mg-stearate +	236	208
0.05 % of Zn-stearate		
0.05 % of Mg-stearate +	180	142
0.05 % of Zn-acetylacetonate		
0.05 % of Mg-stearate +	254	196
0.05 % of Mg-oxide		
0.05 % of Mg-stearate +	158	143
0.05 % of Zn-oxide		
0.05 % of Mg-stearate +	252	. 181.
0.05 % of Mg-hydroxide		

0.05 % of Zn-stearate +	216	193	
0.05 % of Mg-acetate	1	133	
0.05 % of Zn-stearate +	240	188	
0.05 % of Mg-oxide	240	100	
0.05 % of Zn-stearate +	228	470	
0.05 % of Mg-hydroxide	226	173	
0.05 % of Mg-acetylacetonate +	228	135	
0.05 % of Zn-acetylacetonate		133	
0.05 % of Mg-acetylacetonate +	256	189	
0.05 % of Mg-oxide	250	109	
0.05 % of Mg-acetylacetonate +	176	136	
0.05 % of Zn-oxide	170	130	
0.05 % of Mg-acetylacetonate +	252	474	
0.05 % of Mg-hydroxide	232	174	
0.05 % of Zn-acetylacetonate +	156	122	
0.05 % of Mg-oxide	100	122	
0.05 % of Zn-acetylacetonate +	83	69	
0.05 % of Zn-oxide	~	09	
0.05 % of Mg-oxide +	146	100	
0.05 % of Zn-oxide	140	123	
0.05 % of Zn-oxide			

Table 4:

Sterically hindered amine compound:

0.05 % of the compound 81)

UV absorber:

0.05 % of the compound of the formula

Polymer and exposure period are different from those used for Table 3.

Coadditiv	T _{0.2 measured} (kLy)	T _{0.2 calculated}
0.2 % of hydrotalcite (*DHT-4A)	185	
0.2 % of Mg-stearate	196	
0.2 % of Mg-oxide	164	
0.1 % of Mg-stearate + 0.1 % of hydrotalcite (*DHT-4A)	254	190.5
0.1 % of Mg-stearate + 0.1 % of Mg-oxide	234	180

Example II: Light stabilization of injection molded 2 mm polypropylene plaques.

100 parts of polypropylene powder (melt flow index: 2.4 g/10 min at 230°C and 2160 g) are blended in a barrel mixer with 0.05 parts of pentaerythrityl tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.05 parts of tris[2,4-di-tert-butylphenyl] phosphite, and the stabilizer system indicated in Tables 5 and 6. Then, the blend is compounded in an extruder at temperatures of 200°-220 °C. The granules obtained on extrusion and granulation are transformed into 2 mm thick plaques at 240°-260°C in an automatic injection molding machine.

The plaques are mounted on sample holders and exposed in a WEATHER-OMETER Ci 65 (black panel temperature 63±2°C, without water-spraying). Periodically, these samples are removed from the exposure apparatus and their carbonyl content is measured with an infrared spectrophotometer. The exposure time corresponding to formation of a carbonyl absorbance of 0.5 is a measure for the stabilizing efficiency of the light stabilizer.

The values obtained are summarized in Tables 5 and 6.

The determination of the synergistic effect of the two coadditivs is carried out as described in Example I.

Table 5:

UV absorber: 0.05 % of the compound of the formula

	T _{0.5 measured} (hours to 0.5 carbonyl absorbance)			
0.05 % of the sterically hindered amine compound	0.1 % of Mg-stearate + 0.1 % of hydrotalcite (*DHT-4A)	0.2 % of Mg-stearate	0.2 % of hydrotalcite	T _{0.5} calculated
Compound 13	3520	3060	1880	2470
Compound 10	3420	3300	2000	2650
Compound 14	3720	3360	1880	2620
Compound 36-b	2700	2700	1620	2160
Compound 36-a	2780	2920	1720	2320
Compound 63	2340	2280	1900	2090
Compound 49-e	2420	2300	1680	1990
Compound 80-a	2540	2320	1920	2120
Compound 49-a-I	2840	3040	1980	2510

Table 6:

UV absorber: 0.05 % of the compound of the formula

	T _{0.5 measured} (hours to 0.5 carbonyl absorbance)			
0.05 % of the sterically hindered amine compound	0.1 % of Mg-stearate + 0.1 % of hydrotalcite (*DHT-4A)	0.2 % of Mg-stearate	0.2 % of hydrotalcite (*DHT-4A)	T _{0.5} calculated
Compound 81	3320	2840	1300	2070
Compound 84-1	2400	2140	1920	2030
Compound 76	2560	2420	2100	2260
Compound 92	2180	2000	2000	2000
Compound 97-II	2160	2000	1360	1680
Compound 101-I	3080	3080	2600	2840
Compound 100-A	2480	2300	2280	2290
Mixture of compounds 96-1 and 96-11	2080	2000	1900	1950

Example III: Light stabilization of polypropylene tapes.

100 parts of polypropylene powder (melt flow index: 2 g/10 min at 230°C and 2160 g) are blended in a barrel mixer with 0.05 parts of pentaerythrityl tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.05 parts of tris[2,4-di-tert-butylphenyl] phosphite, 0.1 parts of Ca stearate, 0.4 parts of titanium dioxide (rutile) and the stabilizer system indicated in Table

7. Then, the blend is compounded in an extruder at temperatures of 180°- 220°C. The granules obtained on extrusion and granulation are transformed into films at 220°-260°C in a second extruder equipped with a flat sheet die. The films are cut into ribbons which are drawn to achieve a stretch ratio of 1:6. The tapes obtained with this procedure are finally 50 µm thick and 2.5 mm wide.

The tapes are mounted without tension on sample holders and exposed in a WEATHER-OMETER Ci 65 (black panel temperature 63±2°C, without water-spraying). Periodically, the tensile strength of the exposed tapes is measured. The exposure time corresponding to a loss of 50 % (T₅₀) of the initial tensile strength is a measure for the stabilizing efficiency of the stabilizer system.

The values obtained are summarized in Table 7.

The determination of the synergistic effect of the two coadditivs is carried out as described in Example I.

Table 7:

	T _{50 measured} (hours to 50 % retained tensile strength)			
Sterically hindered	0.05 % of	Ţ		
amine compound	Mg-stearate			•
	+	0.1 % of	0.1 % of	
	0.05 % of	Mg-stearate	hydrotalcite	T _{50 calculated}
	hydrotalcite		(*DHT-4A)	
	(°DHT-4A)			
0.05 % of the compound 13	2440	1150	1920	1535
0.10 % of the compound 10	7200	2760	4300	3530
0.20 % of the compound 14	15000	7000	10000	8500

Example IV: Light stabilization of polypropylene copolymer films.

100 parts of unstabilized polypropylene copolymer powder (melt flow index: 3.8 g/10 minutes at 230°C and 2160 g) are homogenized at 200°C for 10 minutes in a [®]Brabender plastograph with 0.05 parts of pentaerythrityl-tetrakis{3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate}, 0.1 parts of tris(2,4-di-tert-butylphenyl) phosphite and the stabilizer system indicated in Tables 8 and 9.

The material thus obtained is compression molded in a laboratory press between two aluminum foils for 6 minutes at 260°C to a 0.5 mm thick film which is cooled immediately to room temperature in a water-cooled press. Samples of 60 mm x 25 mm are cut out of these 0.5 mm films and are exposed in a WEATHER-OMETER Ci 65 (black panel temperature 63±2°C, without water-spraying). Periodically, these samples are removed from the exposure apparatus and their carbonyl content is measured with an infrared spectrophotometer.

The exposure time corresponding to formation of a carbonyl absorbance of 0.1 is a measure for the stabilizing efficiency of the stabilizer system. The values obtained are summarized in the following Tables 8 and 9.

The determination of the synergistic effect of the two coadditivs is carried out as described in Example I.

Table 8:

0.1 % of Ca stearate

	T _{0.1 med}		·)	
0.1 % of the sterically hindered amine compound	0.05 % of Mg stearate + 0.05 % of hydrotalcite (*DHT-4A)	0.1 % of Mg stearate	0.1 % of hydrotalcite (*DHT-4A)	T _{0.1} calculated
Compound 84-1	3260	2100	3340	2720
Compound 84-2	2480	2060	2680	2370
Compound 97-II	2600	2520	2560	2540
Compound 99-I	2040	1580	2340	1960
Compound 99-II	1300	900	1410	1155
Compound 100-A	3760	3200	3460	3330
Mixture of the compounds 96-I and 96-II	2900	2480	3120	2800
Compound 99-III	840	570	930	750

Table 9:

: :

0.1 % of Ca stearate

T_{0.1 measured}

(hours to 0.1 carbonyl absorbance)

0.1 % of the sterically hindered amine compound	0.05 % of Mg stearate + 0.05 % of hydrotalcite (*DHT-4A)	0.1 % of Mg stearate	0.1 % of hydrotalcite	T _{0.1 calculated}
Compound 13	6800	6960	6120	6540
Compound 14	5880	5480	5920	5700
Compound 63	3140	2600	3480	3040
Compound 36-b	4000	3760	3200	3480
Compound 80-a	3400	2900	2700	2800
Compound 49-d	5080	4720	4800	4760
Compound 49-a-l	6520	6760	5840	6300
Compound 49-a-II	6560	5840	5640	5740
Compound 5	8040	8200	7520	7860
Compound 105	3440	2920	3320	3120
Compound 36-d	3160	3080	2980	3030
Compound 69-a	2780	2320	2580	2450

Example V: Light stabilization of high density polyethylene films.

100 parts of unstabilized high density polyethylene powder (density: 0.964 g/cm³, melt flow index: 5.0 g/10 minutes at 190°C and 2160 g) are homogenized at 180°C for 10 minutes in a [®]Brabender plastograph with 0.03 parts of octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate, and the stabilizer system indicated in Table 10.

The material thus obtained is compression molded in a laboratory press between two aluminum foils for 6 minutes at 210°C to a 0.5 mm thick film which is cooled immediately to room temperature in a water-cooled press. Samples of 60 mm x 25 mm are cut out of these 0.5 mm films and are exposed in a WEATHER-OMETER Ci 65 (black panel temperature 63±2°C, without water-spraying). Periodically, these samples are removed from the exposure apparatus and their carbonyl content is measured with an infrared spectrophotometer.

The exposure time corresponding to formation of a carbonyl absorbance of 0.1 is a measure for the efficiency of the stabilizer system. The values obtained are summarized in Table 10.

The determination of the synergistic effect of the two coadditivs is carried out as described in Example I.

Table 10:

	T _{0.1 measured} (hours to 0.1 carbonyl absorbance)			
0.1 % of the sterically hindered amine compound	0.05 % of Mg stearate + 0.05 % of hydrotalcite (*DHT-4A)	0.1 % of Mg stearate	0.1 % of hydrotalcite (*DHT-4A)	T _{0.1} calculated
Compound 81	10160	9160	4720	6940
Compound 84-1	16270	15930	13590	14760
Compound 101-I	18660	18180	15580	16880
Compound 13	10580	10810	5110	7960

Example VI: Light stabilization of high density polyethylene films.

100 parts of high density polyethylene powder (density: 0.961 g/cm³; melt flow index: 6.0 g/10 minutes at 190°C and 2160 g) stabilized with 0.05 parts of octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate and 0.05 parts of bis{2,4-di-tert-butylphenyl}-pentaerythrityl diphosphite are homogenized at 180°C for 10 minutes in a ®Brabender plastograph with the stabilizer system indicated in Table 11.

The material thus obtained is compression molded in a laboratory press between two aluminum foils for 6 minutes at 210°C to a 0.5 mm thick film which is cooled immediately to room temperature in a water-cooled press. Samples of 60 mm x 25 mm are cut out of these 0.5 mm films and are exposed in a WEATHER-OMETER Ci 65 (black panel temperature 63±2°C, without water-spraying). Periodically, these samples are removed from the exposure apparatus and their carbonyl content is measured with an infrared spectrophotometer.

The exposure time corresponding to formation of a carbonyl absorbance of 0.1 is a measure for the efficiency of the stabilizer system. The values obtained are summarized in Table 11.

The determination of the synergistic effect of the two coadditivs is carried out as described in Example I.

Table 11:

	T _{0.1 messured} (hours to 0.1 carbonyl absorbance)			
0.1 % of the sterically hindered amine compound	0.05 % of Mg stearate + 0.05 % of hydrotalcite (*DHT-4A)	0.1 % of Mg stearate	0.1 % of hydrotalcite (*DHT-4A)	To.1 calculated
Compound 84-1	10560	7760	10960	9360
Compound 101-I	2800	1160	3400	2280
Compound 100-A	10160	8720	11280	10000

Compound 13	4160	3480	4480	3980
				l i

Example VII: Light stabilization of polypropylene homopolymer films.

100 parts of unstabilized polypropylene powder (melt flow index: 3 g/10 minutes at 230°C and 2160 g) are homogenized at 200°C for 10 minutes in a Brabender plastograph with 0.05 parts of pentaerythrityl tetrakis{3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate}, 0.1 parts of tris{2,4-di-tert-butylphenyl} phosphite and the stabilizer system indicated in Tables 12 and 13.

The material thus obtained is compression molded in a laboratory press between two aluminum foils for 6 minutes at 260°C to a 0.5 mm thick film which is cooled immediately to room temperature in a water-cooled press. Samples of 60 mm x 25 mm are cut out of these 0.5 mm films and are exposed in a WEATHER-OMETER Ci 65 (black panel temperature 63±2°C, without water-spraying). Periodically, these samples are removed from the exposure apparatus and their carbonyl content is measured with an infrared spectrophotometer.

The exposure time corresponding to formation of a carbonyl absorbance of 0.1 is a measure for the efficiency of the stabilizer system. The values obtained are summarized in Tables 12 and 13.

The determination of the synergistic effect of the two coadditivs is carried out as described in Example I.

Table 12:

T_{0.1 measured}
(hours to 0.1 carbonyl absorbance)

0.1 % of the sterically hindered amine compound	0.05 % of Mg stearate + 0.05 % of hydrotalcite (*DHT-4A)	0.1 % of Mg stearate	0.1 % of hydrotalcite (*DHT-4A)	T _{0.1} calculated
Compound 81	2120	2440	970	1705
Compound 84-1	1600	1560	1510	1535
Compound 101-I	2520	2360	1980	2170

<u>Table 13:</u>

UV absorber: 0.1 % of
$$C(CH_3)_3$$
 $C(CH_3)_3$

	T _{0.1 measured}			
	(hours to 0.1 carbonyl absorbance)			
0.1 % of the sterically hindered amine compound	0.05 % of Mg stearate + 0.05 % of hydrotalcite (*DHT-4A)	0.1 % of Mg stearate	0.1 % of hydrotalcite (*DHT-4A)	T _{0.1 calculated}
Compound 81	3160	3160	1540	2350
Compound 84-1	2420	2440	2160	2300
Compound 101-I	3220	3300	2860	3080
Compound 100-A	3660	2700	2580	2640

Claims:

- 1. A stabilizer mixture containing
- (A) a sterically hindered amine compound, and
- (B) two different compounds selected from the group consisting of an organic salt of Zn, an inorganic salt of Zn, an organic salt of Mg and an inorganic salt of Mg; the weight ratio of the two different compounds being 1:10 to 10:1; with the provisos that
- (1) the stabilizer mixture is essentially free of perchloric acid, and
- (2) the two compounds in component (B) are different from the combination ZnO and Zn stearate and the combination ZnO and hydrotalcite.
- 2. A stabilizer mixture according to claim 1 wherein the sterically hindered amine compound corresponds to a compound containing at least one group of the formula (I) or (II)

in which G is hydrogen or methyl, and

G₁ and G₂, independently of one another, are hydrogen, methyl or together are a substituent =O.

3. A stabilizer mixture according to claim 1 wherein the sterically hindered amine compound corresponds to

with m₁ being a number from 2 to 50,

with m4 being a number from 2 to 50,

with m₄ being a number from 2 to 50,

with m_4 being a number from 2 to 50,

with m_{16} being a number from 2 to 50,

with m₁₆* being a number from 2 to 50,

with m₁₇ being a number from 1 to 50,

with m₁₉ being a number from 1 to 50,

with m_{19} being a number from 1 to 50,

with $m_{\mbox{\tiny 19}}$ being a number from 1 to 50,

a product obtainable by reacting an intermediate product, obtained by reaction of a polyamine of the formula (100a-I) with cyanuric chloride, with a compound of the formula (100b-I),

(100b-l),

$$H_2N$$
 —— (CH_2) $\frac{1}{3}$ NH —— (CH_2) $\frac{1}{2}$ NH (CH_2) $\frac{1}{3}$ $(100a-1)$

with m₂₁ being a number from 1 to 50,

or

4. A stabilizer mixture according to claim 1 wherein

the two different compounds of component (B) are selected from the group consisting of hydrotalcite, dolomite, Zn-hydroxide-carbonate, Mg-hydroxide-carbonate, Zn-oxide, Mg-oxide, Zn-hydroxide, Mg-hydroxide, Zn-stearate, Mg-stearate, Zn-acetylacetonate, Mg-acetylacetonate, Zn-acetate and Mg-acetate.

A stabilizer mixture according to claim 1 wherein the two different compounds in component (B) are
 Mg-stearate and hydrotalcite,
 Zn-stearate and hydrotalcite,
 Mg-stearate and Zn-stearate,
 Zn-stearate and Mg-oxide, or
 Mg-stearate and Mg-hydroxide.

- 6. A stabilizer mixture according to claim 1, containing additionally(C1) a pigment or(C2) an UV absorber or(C3) a pigment and an UV absorber.
- 7. A stabilizer mixture according to claim 6 wherein the pigment is titanium dioxide, zinc oxide, carbon black, cadmium sulfide, cadmium selenide, chromium oxide, Iron oxide, lead oxide, an azo pigment, an anthraquinone, a phthalocyanine, a tetrachloroisoindolinone, a quinacridone, an isoindoline, a perylene or a pyrrolopyrrole.
- 8. A stabilizer mixture according to claim 6 wherein the UV absorber is a 2-(2'-hydroxyphenyl)benzotriazole, a 2-hydroxybenzophenone, an ester of substituted or unsubstituted benzolc acid, an acrylate, an oxamide, a 2-(2-hydroxyphenyl)-1,3,5-triazine, a monobenzoate of resorcinol or a formamidine.
- 9. A stabilizer mixture according to claim 1 which additionally contains an organic salt of Ca or an inorganic salt of Ca.

- 10. A composition comprising an organic material subject to degradation induced by light, heat or oxidation and a stabilizer mixture according to claim 1; with the proviso that the composition is essentially free of perchloric acid.
- 11. A composition according to claim 10 wherein the organic material is a polyolefin.
- 12. A composition according to claim 10 wherein the organic material is polyethylene, polypropylene, a polyethylene copolymer or a polypropylene copolymer.
- 13. A method for stabilizing an organic material against degradation induced by light, heat or oxidation, which comprises incorporating into the organic material a stabilizer mixture according to claim 1; with the proviso that the organic material is essentially free of perchloric acid.





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d: 1 to 13

Examiner:

Miss M M Kelman

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): C3K KCZ

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Other: ONLINE: EDOC, PAJ

Documents considered to be relevant:

Category	Identity of document and relevant passage			
х	EP 0421933 A1	CIBA-GEIGY see Examples 1 to 9	1,2,3,4,5, 6,7,9,10,1 3	
х	EP 0290388 A2	CIBA-GEIGY see the claims and page 18, lines 4 to 5	1,2,3,4,10 ,11,12,13	
х	EP 0212559 A2	ADEKA ARGUS see Examples 15 to 26, Control Examples 4 and 5 in Table III and Control Example 3 in Table IV	1,2,3,6,9, 10 and 13	
х	US 5283273 A	CIBA-GEIGY see the claims and column 21, lines 38 to 52	1,2,6,10,1 3	
х	US 5037870 A	CIBA-GEIGY see column 5, lines 15 to 19	1,2,3,4,10 ,11,12,13	
х	US 5025051 A	FERRO CORPORATION see Comparative Examples 10,11,12,15,16, and 17	1,2,3,4,5, 6,7,10,13	
x	US 5025050 A	ETHYL CORPORATION see the claims	1,2,3,4,6, 8,10,13	

- X Document indicating lack of novelty or inventive step
 Y Document indicating lack of inventive step if combined with one or more other documents of same category.
- A Document indicating technological background and/or state of the art.

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Examiner:

Miss M M Kelman 13 April 1999

Claims searched: 1 to 13 Date of search:

Сатедоту	Identity of document and relevant passage		
х	US 4929652 A	CIBA-GEIGY see the claims and column 22, lines 59 to 69	1,2,4,6,8, 10,11,12,1 3

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